

Compliance of Copper Beryllium and ToughMet® 3 Copper-Nickel-Tin Alloys to NACE MR0175/ISO 15156

The purpose of the NACE MR0175/ISO 15156 standard is to provide a set of guidelines for the use of material in sour (H₂S) service. Nickel and steel alloys are prone to cracking in such applications. For these and other alloys, the standard lists the service conditions that are known to cause cracking problems, and suggests maximum hardness levels to avoid cracking. Copper alloys are generally immune to these cracking problems and thus have not been specifically addressed by name in this standard. However, copper alloys in general (including copper beryllium and ToughMet 3 copper nickel tin) are listed in the standard as being acceptable for use in sour service.

NACE COMPLIANCE

By definition, the NACE MR0175/ISO 15156 standard addresses the selection and use of materials in oil and gas production where the presence of H₂S in the environment creates a potential for failure by cracking. In order to be listed in the standard, materials must be shown to resist H₂S cracking, either by experience or test data. The standard cautions that this test data or experience has been obtained in very specific environments, and that an individual service environment may be very different. In other words, a material that is listed as being acceptable for service in one environment may fail dramatically in another for which no experience or test data exists. Furthermore, materials that are not listed in the standard may also be used, if the appropriate test data is available. The standard urges the person making the material selection to look at the available test data before making a decision.

COPPER ALLOYS

Copper-based alloys are listed in Part 3; Annex A; Section 12 of the standard. The standard notes, “Copper-based alloys have been used without restriction on temperature, [partial pressure of hydrogen sulfide (H₂S)], Cl⁻, or in situ pH in production environments.” The two notes in the section indicate that copper alloys may undergo accelerated weight loss in sour environments, and that some copper alloys may show sensitivity to galvanically induced hydrogen stress cracking.^[1] However, the test data listed later in this publication shows that CuBe and ToughMet 3 will perform as well as or better in terms of weight loss and cracking resistance than some of the nickel

and steel based alloys specifically mentioned in the standard.

CORROSION TESTING

The standard indicates materials not listed within it may be used, if appropriate laboratory test data show adequate resistance to cracking. The recommended tests first determine if cracking occurs in simulated oilfield environments. If the samples do not crack, the corrosion rate of the metal in the test solution is calculated. (See Figure 1 and Table 1.)

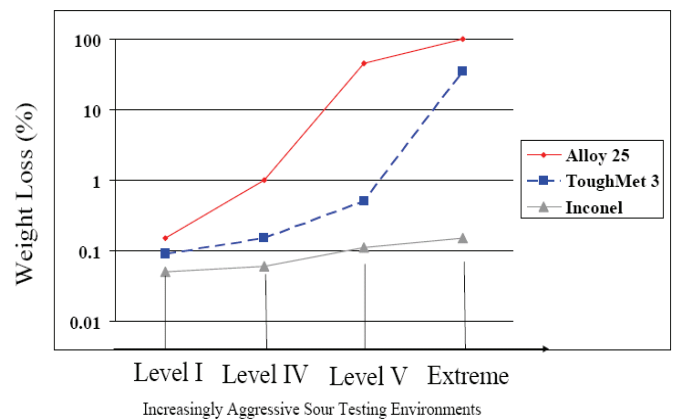


Figure 1 – Corrosion Rates of ToughMet 3 and Alloy 25 copper beryllium in simulated sour environments.

NACE standard TM0177-2005 is used to determine resistance of materials to sulfide stress cracking and stress corrosion cracking in the presence of hydrogen sulfide at room and elevated temperatures, respectively. A sample of

the test metal is stressed in tension or bending in one of four methods and is immersed in one of three test solutions. The reported test results are typically the highest stress level that did not produce cracking in 720 hours. [2]

NACE Standard TM0198-2004 covers testing that evaluates the cracking resistance of materials subjected to very slowly increasing tensile stress in test solutions containing hydrogen sulfide, carbon dioxide, and brine. Upon fracture, the test specimen is examined for evidence of stress corrosion cracking. Furthermore, the tensile properties obtained in the test solution are compared to those in air to see how they are affected by the simulated drilling environment. [3]

COPPER BERYLLIUM AND TOUGHMET® TEST DATA

The test results for copper beryllium and ToughMet 3 have been presented at various NACE Corrosion Conferences. Copies of the proceedings of these conferences are available from NACE.

Paper 220 at Corrosion 84 showed that Alloy 25 copper beryllium did not crack in simulated oilfield environment, while all of the nonmagnetic stainless steels that were tested cracked within 30 days. Alloy 25 showed acceptably low corrosion rates up to 149°C (300°F) in environments with up to 1% H₂S, and up to 66 C with 10% H₂S in all product forms. [4]

Paper 171 at Corrosion 86 demonstrates that copper beryllium shows resistance, but not complete immunity, to hydrogen charging. It was unaffected at light charging, but moderately effected at heavy charging. N05500 nickel-copper alloy and N09925 nickel-iron-chromium alloy experienced substantial embrittlement under both charging conditions. [5]

Paper 303 at Corrosion 87 shows that Alloy 25 copper beryllium, N05500 nickel-copper and N07031 nickel-iron-chromium alloys are immune to chloride stress corrosion cracking, per the ASTM G36-73 test method. (There were no failures after 1000 hours in boiling 45% MgCl solution, at stress levels up to 100% of the yield strength.) The austenitic stainless steel alloys failed within 200 hours at stress levels of 25% of the yield strength. The performance of N09925 fell between these two extremes. [6]

Paper 69 at Corrosion 88 demonstrates that Alloy 25 copper beryllium is immune to chloride stress corrosion cracking (no failures in 1000 hours), with low corrosion rates, independent of the test fluid's temperature and oxygen content. N09925 and various steel alloys failed at different time intervals depending on the oxygen content of the test fluid. [7]

Paper 298 at Corrosion 2004 shows that ToughMet 3 is resistant to stress corrosion cracking and hydrogen embrittlement in synthetic seawater slow strain rate testing. There was no reduction of load carrying capability or change in failure mode under all conditions, including freely corroding and various galvanic coupling situations. Low corrosion rates were observed, similar to other copper nickel alloys. No pitting corrosion was observed. ToughMet 3 is galvanically similar to other copper-nickel alloys. [8]

Paper 100 at Corrosion 2007 shows that ToughMet 3 TS temper possesses nearly the same level corrosion resistance that the CX and AT tempers do. [9]

COPPER BERYLLIUM ADVANTAGES

Alloy 25 copper beryllium is anti-galling when in contact with stainless steels and other alloys. For oilfield applications, it has sufficient resistance to wear and erosion. Its elastic modulus is approximately 33% lower than steel, resulting in high bending resilience. Alloy 25 is non-magnetic with a relative permeability < 1.001. It has very good machinability compared to other materials, particularly to steel and nickel alloys. Alloy 25 copper beryllium complies with NACE MR0175/ISO 15156, with no restriction on hardness. NACE standard testing indicates that there is no susceptibility to chloride (brine / seawater / completion fluid) cracking or pitting corrosion, and it is immune to hydrogen embrittlement cracking in sour wells. It is also not subject to biofouling. Alloy 25 can also be a substantial cost saving material when compared to nickel alloys. [8]

Alloy 25 has been used successfully in the following oilfield applications:

- Drill bit bearings
- Non-magnetic motor flex drive shafts
- Non-Magnetic pressure housings for downhole electronics and batteries in Measurement While Drilling (MWD) tools, Logging While Drilling (LWD) tools, and Horizontal

Materion Brush Performance Alloys

6070 Parkland Boulevard
Mayfield Heights, OH 44114 USA
phone: 216.486.4200 fax: 216.383.4005
e: BrushAlloys-Info@Materion.com

TECHNICAL INQUIRIES

ph: 800.375.4205

MATERION CORPORATION

www.materion.com

AT0054/0311

©2011 Materion Brush Inc.

Directional Drilling (HDD) steering tools

- Drill string non-magnetic, non-galling downhole disconnect collars
- Subsea valve gates, actuators, locking rings and seats

TOUGHMET 3 ADVANTAGES

ToughMet 3 provides high strength and strain tolerance (fatigue life). It possesses excellent machinability relative to nickel and steel alloys, and provides a substantial cost savings. It is also nonmagnetic, with a relative permeability similar to that of copper beryllium (<1.001). It possesses low friction when in contact with other metals, and is more resistant to galling and scuffing than most other oilfield materials.

ToughMet 3 complies with NACE MR0175 and ISO 15156 panels for unrestricted Sour Well Service per Section 4 including notations (tested up to 150 C NACE Level V). NACE standard testing indicates that ToughMet 3 shows resistance to amine-based fluid corrosion (no embrittlement or accelerated weight loss). It is resistant to seawater and brine corrosion, with a general corrosion rate less than 0.001" per year, and no susceptibility to hydrogen embrittlement, including notched areas. No pitting or corrosion cracking occurred when tested in high concentrations of chlorides or bromides. It is not subject to biofouling. When pre-stressed to 90% of Yield Strength for 30 days immersion in NACE Levels I, IV, and V test solutions, it shows a minimal general corrosion rate (1-3 mil per year) and no sulfide stress corrosion cracking.

ToughMet has been used successfully in the following oilfield applications:

- Well Perforation Gun explosive charge liners
- Drill string centralizers, stabilizers, and shock collars
- Rotary steerable drilling tool hardware including housings, actuators, bearings, pistons, power transmission joints, drive shafts, etc. in control and bias units
- Sucker rods and polished rods
- Subsea well control manifold hydraulic connectors
- Sour service MWD, LWD pressure housings for electronics and batteries
- Expandable well casing sand screen tool bearings
- Sour service subsea valve actuators, lifting nuts, other mechanical bearings
- Kelly valve seats
- Reservoir completion and formation isolation valve

indexers

- Non-magnetic mud motor stators
- Rotor shaft bearings for Electric Submersible Pumps (ESP's)

REFERENCES

1. NACE MR0175/ISO 15156-3:2003(E) "Petroleum and natural gas industries – materials for use in H₂S-containing environments in oil and gas production – Part 3: Cracking-resistant CRAs (corrosion-resistant alloys) and other alloys" ©2003 NACE/ANSI/ISO
2. NACE Standard TM0177-2005 "Laboratory Testing of Metals for Resistance to Sulfide Stress Cracking and Stress Corrosion Cracking in H₂S Environments" ©2005 NACE International
3. NACE Standard TM0198-2004 "Slow Strain Rate Test Method for Screening Corrosion-Resistant Alloys (CRAs) for Stress Corrosion Cracking in Sour Oilfield Service" ©2004 NACE International
4. J. Booker, W.R. Crib, J.C. Turn Jr., R.D. Kane "Corrosion Behavior of Beryllium Copper and other Nonmagnetic Alloys in Simulated Drilling Environments" Corrosion/84, Paper 220, Cypress, TX, ©NACE International 1984
5. John C Turn, Jr., John O. Ratka, "The Mechanical Behavior of Hydrogen Charged Beryllium Copper" Corrosion/86, Paper 171, Houston, TX, ©NACE International 1986
6. John C Turn, Jr., "The Chloride Stress Corrosion Cracking Behavior of Beryllium Copper and other Nonmagnetic Drill Collar Alloys" Corrosion/87, Paper 303, San Francisco, CA, ©NACE International 1987
7. John C Turn, Jr., "The Effect of Oxygen and Temperature on Chloride Stress Corrosion Cracking of Beryllium Copper and other Nonmagnetic Alloys in a Simulated Chloride Drilling Environment" Corrosion/88, Paper 69, St. Louis, MO, ©NACE International 1988
8. J. O. Ratka, M.N. Malingas "Corrosion Evaluation of a High Performance Cu-Based Alloy for Seawater Applications" Corrosion/2004, Paper 04298, Houston, TX, ©NACE International 2004

Materion Brush Performance Alloys

6070 Parkland Boulevard
Mayfield Heights, OH 44114 USA
phone: 216.486.4200 fax: 216.383.4005
e: BrushAlloys-Info@Materion.com

TECHNICAL INQUIRIES

ph: 800.375.4205

MATERION CORPORATION

www.materion.com

AT0054/0311

©2011 Materion Brush Inc.

9. W. Raymond Cribb “Sour Service Testing of High Strength TS Temper CuNiSn Alloy (UNS C72900) Corrosion/2007, Paper 07100, Nashville, TN, ©NACE International 2007

SAFE HANDLING OF COPPER BERYLLIUM

Handling copper beryllium in solid form poses no special health risk. Like many industrial materials, beryllium-containing materials may pose a health risk if recommended safe handling practices are not followed. Inhalation of airborne beryllium may cause a serious lung

disorder in susceptible individuals. The Occupational Safety and Health Administration (OSHA) has set mandatory limits on occupational respiratory exposures. Read and follow the guidance in the Material Safety Data Sheet (MSDS) before working with this material. For additional information on safe handling practices or technical data on copper beryllium, contact Materion Brush Performance Alloys, Technical Service Department at 1-800-375-4205.

ToughMet® is a registered trademark of Materion Brush Inc.

| | | NACE Environment | | | | |
|--|--|------------------|-----------|--------------|-----------|-----------|
| | | Level I | Level II | Level IV | Level V | Level VII |
| Temperature °F (C) | | 23 | 23 | 90 | 150 | 205 |
| H ₂ S Partial Pressure in psi (MPa) | | 0 | Saturated | 0.43 (0.003) | 101 (0.7) | 508 (3.5) |
| CO ₂ Partial Pressure in psi (MPa) | | 0 | | 101 (0.7) | 203 (1.4) | 508 (3.5) |
| Acetic Acid (%) | | 0 | 0.5 | | | |
| NaCl (%) | | 5 | 5 | 15 | 15 | 25 |

| Alloy | Temper | Hardness HRC max. | NACE Environment | | | | |
|-------------|---------|-------------------|------------------|----------|-----------|-----------|-----------|
| | | | Level I | Level II | Level IV | Level V | Level VII |
| ToughMet® 3 | CX | 33 | <0.5 (<13) | 0.7 (18) | 1.3 (33) | 6.9 (175) | |
| ToughMet® 3 | TX (AT) | 32 | <0.5 (<13) | 0.8 (20) | 1.3 (33) | 3.7 (94) | |
| ToughMet® 3 | TS | 37 | <0.5 (<13) | 1.1 (28) | 4.0 (100) | Cracking | Cracking |

Table 1 – Corrosion Rates of ToughMet 3 in Simulated Drilling Environments